Topological Effects of Knots in Polymers

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We present a phenomenological theory of the static and dynamic effects of knots in polymers. The theory is tested by Monte Carlo simulations using the kink-jump-crankshaft and Berg-Foerster-Aragao de Carvalho-Caracciolo-Froehlich algorithms. A long time relaxation mode is discovered in the dynamics of knotted polymers that is not predicted by the Rouse model. This mode is not present in the trivial knot and appears to be the result of purely topological interactions.

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The first scientific approach to the study of knots began in the 19th century with the efforts of Kelvin and Tait [1]. Mathematicians have made much progress understanding knots in a topological framework in the 20th century, and deep connections between statistical mechanics and knot topological invariants have recently been discovered [2]. Experimentally, chemical knots remained a curiosity until the work of Wang [3], Wasserman and Cozzarelli [4], and others in elucidating the role of topology in the life processes of DNA. With the advent of powerful numerical techniques, physicists have made inroads toward answering some basic theoretical questions about knots, such as discovering the probability that a polymer is knotted [5] and the distribution of random knots [6]. However, the effects of a fixed knot type on the static and dynamic properties of a particular polymer are less well understood [7,8].

The topological effects of fixed knots in single polymers have important ramifications in biology, where the topology of DNA is nonrandom and plays a crucial role in life processes; there are enzymes whose function is to systematically change the knot type of circular DNA [9]. The experimental study of knotted DNA is mature [4], and it is well established that the mobility of a knot depends on the knot type. However, this purely experimental observation has not been explained except to hypothesize that topological constraints reduce the radius of gyration of knotted polymers, leading to a higher mobility [4]. Topological effects have come into play in other areas of polymer physics, but rigorous progress has been difficult, and the most successful theories make *ad hoc* assumptions about the role of topology. One of the most famous such theories is the Edwards–de Gennes reptation tube model [10].

Although there are connections between knot invariants and various models in statistical mechanics, knot invariants are algebraic quantities and are difficult to treat with the tools of analysis. In this Letter, we follow the example of Edwards and de Gennes and develop a crude phenomenological model of the effects of knot complexity on the static and dynamic properties of knots. The reptation tube model is successful because it relates topological effects to geometry, making the problem tractable to analysis. We use that philosophy, and our model tries to relate topological constraints to geometric constraints. The model predicts the scaling law behavior of the radius of gyration and relaxation time of polymers as a function of knot complexity. We tested the theory with Monte Carlo simulations and report the first systematic investigation of knot size as a function of knot complexity. We also simulated the dynamics of a fixed length polymer to study the relationship between topology and relaxation time.

One measure of knot complexity is the minimum number of self-crossings the knot has when projected into a plane. This is clearly a topological invariant, albeit a weak one (it does not distinguish very well between knot types; there are 166 knots with 10 crossings). It also forms the basis for a system of classifying knots: the standard notation for uniquely identifying a knot is C_K, where C is the number of crossings and K is an index to a particular knot [11]. We have chosen this as the starting point of our theory since the mobility assay for DNA differentiates based on the number of crossings: Knots with the same number of crossings have the same mobility [4].

By studying an easy knot such as the trefoil 3_1 (Fig. 1), with a small leap of the imagination one sees that it is effectively made up of three interlocking loops. The "local" structure is a loop encircling a free strand. When the knot is projected onto a plane, the free strand topological constraint gets mapped to an essential crossing. Our idealized picture of a knot is then as a

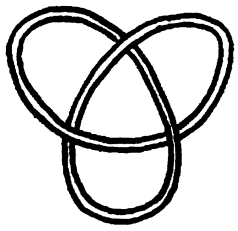

FIG. 1. The trefoil 3_1.

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set of interlocked loops, where the number of loops is determined by the number of essential crossings.

A knot of length N and C essential crossings is considered as C loops, each of length N/C. Each loop then has radius of gyration $R_{g,\mathrm{loop}} \propto (N/C)^{\nu}$ and volume $V_{\mathrm{loop}} \propto R^3_{g,\mathrm{loop}} \propto (N/C)^{3\nu}$. Excluded volume effects will cause a mutual repulsion, and the minimum energy configuration will balance the repulsive force with the attractive force of the loop linkage. Since the loops are free to slide along each other, they have the ability to distribute themselves in space. The total volume will then be proportional to the sum of the individual volumes where the coefficient will have to take into account some degree of overlap between the loops:

$$V \propto CV_{\mathrm{loop}} \propto C(N/C)^{3\nu} = N^{3\nu}C^{1-3\nu}. \quad (1)$$

But the volume must go as the cube of the radius of gyration of the knot:

$$R_g \propto V^{1/3} \propto N^{\nu}C^{1/3-\nu} = N^{3/5}C^{-4/15}, \quad (2)$$

where in the last step we used the Flory value $\nu = 3/5$ in three dimensions. The radius of gyration depends weakly upon the complexity; it does decrease, as one expects from the experimental mobility evidence. Additionally, independent of the knot complexity, we have retained the fundamental scaling law of polymers that $R_g \propto N^{\nu}$.

One can also calculate the effects of a knot on the dynamic relaxation of a polymer. The Rouse model describes polymer relaxation in the absence of hydrodynamic interactions between monomers, and a heuristic derivation of the relaxation time [12] can be modified for our purposes. The argument uses the idea that the fundamental relaxation time is a long distance rotational relaxation time and is determined when the center of mass of the polymer has moved a distance on order of the radius of gyration. This is interpreted in terms of local monomer solvent interactions: Each such interaction changes the center of mass by a factor of $1/N$. Since these interactions are not coherent, they add up as a random walk. Since they are happening simultaneously, in the relaxation time τ there are τN such displacements. Then we have

$$\left(\frac{1}{N}\right)^2 \tau N \propto R_g^2 \propto (N^{\nu}C^{1/3-\nu})^2 \quad (3)$$

and

$$\tau \propto N^{2\nu+1}C^{2/3-2\nu} = N^{2.2}C^{-0.53}. \quad (4)$$

The algorithm of Berg, Foerster, Aragao de Carvalho, Caracciolo, and Froehlich (BFACF) [7,13] is useful for studying the static behavior of knots and has been shown to be ergodic within a fixed knot type [14]. For dynamic behavior, the Verdier-Stockmayer kink-jump algorithm combined with a crankshaft motion (KJC) [12] better imitates the local motion of polymers since it is length preserving. Although KJC is in principle nonergodic [15], the effects of the nonergodicity appear to be small [8,12]. Both BFACF and KJC were implemented in a fast lattice algorithm [8]. We iterated 10^8 BFACF attempts per knot after thermalization for static quantities, while for dynamic quantities we iterated 10^9 KJC attempts per knot after thermalization.

To test the proposed scaling laws (2) and (4), we investigated the dependence of knot size on complexity. Figure 2 shows the radii of gyration for knots of lengths 100 and 400. We exhaustively computed all knots up to and including 8_1. Three representatives with 8 crossings and six representatives with 10 crossings were arbitrarily chosen to get data on knots with higher numbers of crossings. As the number of knots is increasing rapidly with the number of crossings, it is not practical to make a comprehensive study. The data were fitted by a power law, and the fitted exponents of -0.235 ($N = 100$) and -0.23 ($N = 400$) are in agreement and close the value of $-4/15 = -0.27$ predicted by Eq. (2).

We measured the dynamic relaxation time in KJC by computing the time correlation function of the radius of gyration $\langle R_g(t)R_g(0)\rangle - \langle R_g^2\rangle$. For the trivial knot ("unknot"), the relaxation time as a function of length ($N = 64-256$) scaled with an exponent of 2.27(.06), in excellent agreement with the Rouse model. However, a surprising result happened when we measured the relaxation of more complicated knots: We found a family of relaxation curves, all with an initial relaxation similar to the unknot, but with a new long time mode (Figs. 3 and 4). This is entirely unexpected; Eq. (4) predicts only a small shift in the relaxation time.

To study the new mode quantitatively, we fit the relaxations by the sum of two exponentials, with

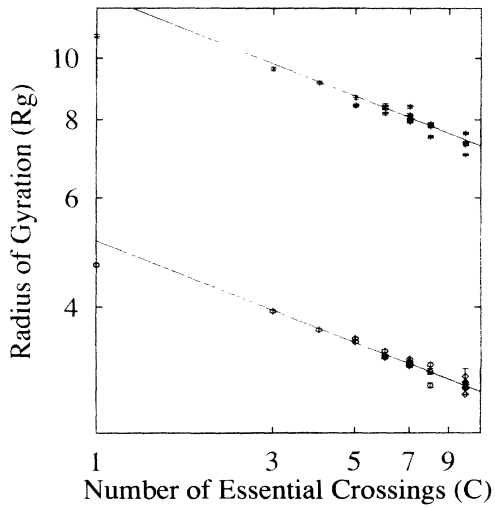

FIG. 2. Scaling of radius of gyration with knot complexity for knots of length $N = 100$ (lower points and line) and $N = 400$ (upper points and line). The unknot has been moved to $C = 1$, since $C = 0$ is singular.

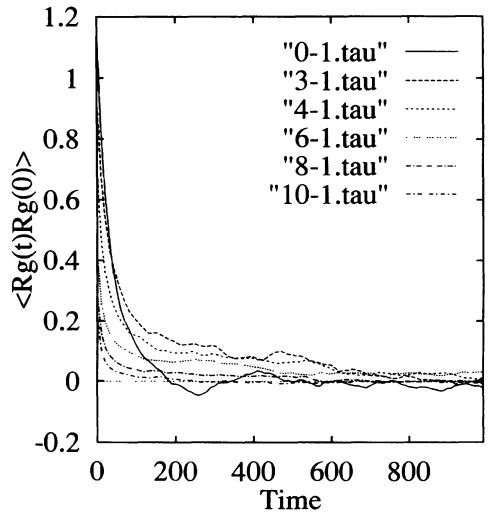

FIG. 3. Relaxation curves for several different knots of length $N = 256$. (Note "3-1.tau" corresponds to 3_1, etc.)

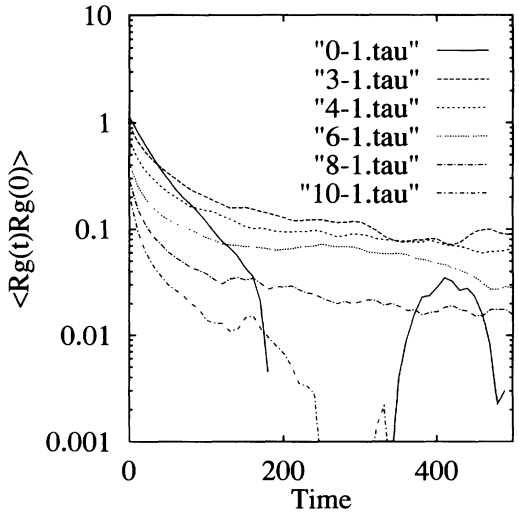

FIG. 4. A semilogarithmic plot of the relaxation curves ($N = 256$).

independent magnitudes and relaxation times (Table I and Fig. 5). In the case of the unknot, the second exponential picked up the second order Rouse mode, whose relaxation time is expected to be $2^{\nu} = 1.5$ times faster and amplitude $2^{1+2\nu} = 4.6$ times smaller. However, for the nontrivial knots, the slowest relaxation time is up to a full order of magnitude slower than the unknot. This relaxation mode appears to be the result of purely topological interactions: it appeared in all five knot types we tested, it did not appear in the unknot for any length we tested, and it remained a feature of 3_1 relaxation as we varied the length. It seems to be outside of the Rouse model, rather than just a shift in the spectrum. The magnitude of the topological mode is smaller than the magnitude of the next fastest mode, and the fundamental relaxation time is up to an order of magnitude longer than the next mode; both observations contradict the Rouse model. The faster modes display a structure consistent with Eq. (4) (inset, Fig. 5).

To test the robustness of the topological mode, we ran Monte Carlo simulations of the knot 3_1 for a variety of lengths and then rescaled the relaxation functions using a data collapse program [8] (Fig. 6). The functions fit well on top of each other, although it is not clear that they are universal. The rescaled times were fitted by a power law (inset, Fig. 6) and appear to go as $\tau \propto N^{2.7(.4)}$, indicating that the full relaxation function may still obey Rouse scaling.

In summary, a theory of the statistical mechanics of knots was presented; it essentially tried to convert topological constraints into geometric constraints. Predictions of the scaling exponents for the radius of gyration and

TABLE I. Fitted values for the knot relaxation functions. The function is $f(t) = b_{\text{short}} \exp(-t/\tau_{\text{short}}) + b_{\text{long}} \exp(-t/\tau_{\text{long}})$.

Knot	τ_{long}	b_{long}	τ_{short}	b_{short}
0_1	45.83(4)	0.9(0.1)	10.5(6)	0.2(0.1)
3_1	343(15)	0.2(0.01)	27(1)	0.7(0.02)
4_1	428(14)	0.2(0.005)	23.2(0.8)	0.5(0.009)
6_1	524(24)	0.1(0.003)	18.6(1)	0.3(0.009)
8_1	271(12)	0.06(0.002)	14.3(0.6)	0.2(0.005)
10_1	78.8(7)	0.06(0.006)	8.6(0.8)	0.159(0.006)

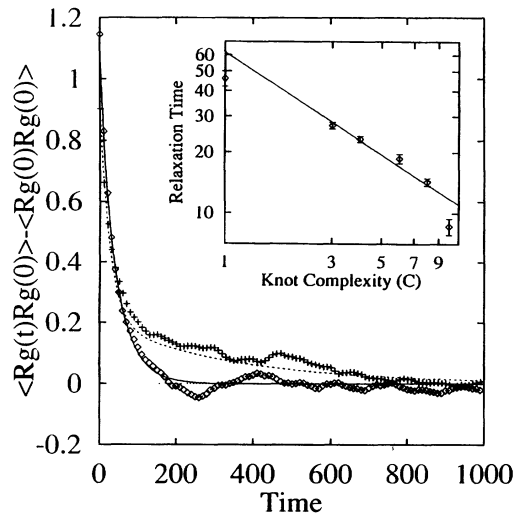

FIG. 5. Sample fits to two exponentials, for the unknot and 3_1. There are slight systematic errors, indicating that the mode concept may be breaking down. Inset: The scaling of nontopological relaxation time with knot complexity is not far from the prediction of Eq. (4); the fitted value of the exponent is 0.7.

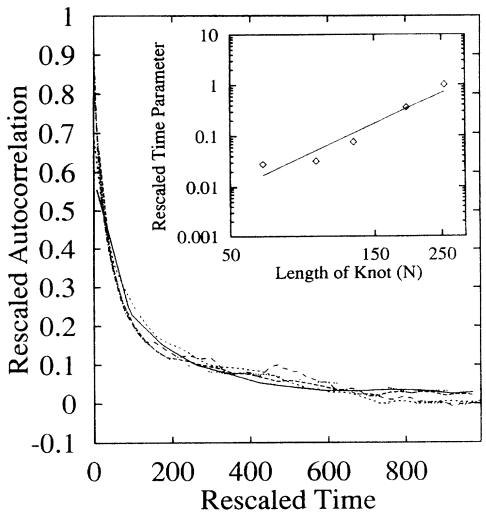

FIG. 6. Relaxation functions of the knot 3_1 (lengths N = 64, 96, 128, 192, 256) that have been data collapsed on top of each other. Inset: The rescaled time parameter on a log-log plot.

relaxation time were derived. The theory was tested against computer simulations and agreed well for the radius of gyration. We discovered a new long time mode in the dynamic relaxation that appears to be purely topological in nature. Rouse scaling of the entire relaxation function appears to hold, and scaling of the nontopological relaxation time as a function of knot complexity is in reasonable agreement with Eq. (4). There is evidence from dynamic light scattering experiments that topological constraints in reptating polymer networks also cause a slow relaxation mode [16]. The results of this Letter support that claim, and it is possible that a knotted polymer undergoes "self-reptating" behavior due to its own topological constraints.

There are many further questions that can be addressed with these techniques. One could use the present results to calculate knot mobility and compare it to experimental gel electrophoresis data. The average radius of gyration can be explored as a new knot invariant. Finally, there are questions about the effects of knots on polymer elasticity which the KJC simulation could be modified to address.

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[1] W. Thompson, Philos. Mag. **34**, 15 (1867); P. G. Tait, in *Scientific Papers* (Cambridge University Press, London, 1898).

[2] *Braid Group, Knot Theory and Statistical Mechanics*, edited by C. N. Yang and M. L. Ge, (World Scientific, New Jersey, 1989).

[3] J. C. Wang, J. Mol. Bio. **55**, 523 (1971).

[4] S. A. Wasserman and N. R. Cozzarelli, Science **232**, 951 (1986).

[5] D. W. Sumners and S. G. Whittington, J. Phys. A **21**, 1689 (1988).

[6] V. V. Rybenkov, N. R. Cozzarelli, and A. V. Vologodskii, Proc. Natl. Acad. Sci. U.S.A. **90**, 5307 (1993).

[7] E. J. Janse van Rensburg and S. G. Whittington, J. Phys. A **24**, 3935 (1991).

[8] S. R. Quake, (to be published).

[9] A. Kornberg, *DNA Replication* (W. H. Freeman and Co., San Francisco, 1980).

[10] M. Doi and S. Edwards, *The Theory of Polymer Dynamics* (Oxford University Press, Oxford, 1992).

[11] D. Rolfsen, *Knots and Links* (Publish or Perish, Inc., Houston, 1990).

[12] K. Kremer and K. Binder, Comp. Phys. Rep. **7**, 259 (1988).

[13] B. Berg and D. Foerster, Phys. Lett. B **106**, 323 (1983); C. Aragao de Carvalho and S. Caracciolo, J. Phys. (Paris) **44**, 323 (1983); C. Aragao de Carvalho, S. Caracciolo, and J. Froehlich, Nucl. Phys. **B215**, 209 (1983).

[14] E. J. Janse van Rensburg and S. G. Whittington, J. Phys. A **24**, 5553 (1991).

[15] N. Madras and A. E. Sokol, J. Stat. Phys. **47**, 573 (1987).

[16] E. J. Amis, P. A. Janmey, J. D. Ferry, and H. Yu, Macromolecules **16**, 441 (1983); M. Eisele and W. Burchard, Macromolecules **17**, 1636 (1984); W. Brown, Macromolecules **17**, 66 (1984).